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Quarterly Technical Summary Report No. 1  
December 1, 1965 to February 28, 1966

RESEARCH ON THE DEFLAGRATION  
OF HIGH-ENERGY SOLID OXIDIZERS

Contract No. AF 49(638)-1645

To

Air Force Office of Scientific Research  
Washington, D. C.

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March 31, 1966

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March 31, 1966

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## I. ABSTRACT

The task of the present program is fundamental research on advanced solid oxidizers with the aim of understanding their self-deflagration. Hydrazine perchlorate and hydrazine diperchlorate have received, of late, most of the attention. The effort during this quarter has been devoted to elucidating some of the chemistry involved in the deflagration process. Toward this end we have carried out a literature review of the thermal behavior of hydrazine and perchloric acid. This was extended to include a review of reactions of chlorine oxides. The kinetics and mechanisms of the latter compounds, it was discovered, are not very well understood. Hence, we have performed some experiments on  $\text{ClO}_2$  and  $\text{ClO}_3$ , two species which seem likely to be important in oxidizers encountered in the program. In particular we have concentrated on the explosive decomposition of  $\text{ClO}_2$ . It was found to explode by a degenerate chain-branching mechanism at all temperatures and pressures above  $54^\circ\text{C}$  and a few tenths of a mm Hg. Very long induction periods were observed, and  $\text{ClO}_3$  was shown to be a critical intermediate. The explosion is promoted by irradiation and by addition of foreign gases.

## II. INTRODUCTION

We are engaged in a general program of research whose goal is the understanding of the factors that govern the nature of the deflagration of composite solid propellants. Our efforts have been devoted to studies of the oxidizer alone, ever since early observations that ammonium perchlorate deflagrated as a monopropellant at rates comparable to those found for propellant formulations containing it (1,2). This suggested that self-deflagration of the oxidizer played an important role in the deflagration of the propellant. Research in this and other laboratories has confirmed this hypothesis. Our early work was concerned with ammonium perchlorate and we have reported on its self-deflagration and other aspects of its chemistry that are pertinent to the deflagration process (3).

Under a recent contract (4), we have extended studies of oxidizers to compounds that are of present and potential interest as energetic ingredients in solid propellants -- namely, hydrazine perchlorate and hydrazine diperchlorate. Approximately one-half of the effort in that program was given to each compound. Each was found to exhibit different chemical behavior and to deflagrate in a manner different from the other and from ammonium perchlorate.

From the research mentioned above, a significant deflagration concept emerged: the mode of gasification in oxidizer deflagration. In ammonium perchlorate (AP) deflagration, gasification is by sublimation with no indication of fusion or melting. In hydrazine perchlorate (HP) deflagration, gasification occurs by nucleate boiling, and a molten layer is very prominent. In hydrazine diperchlorate (HDP) deflagration, gasification is principally by chemical attack. The gasification concept has been discussed in more detail in Ref. 5.

Gasification by chemical attack is not unique to HDP but occurs also in hydrazine nitroform (HNF) deflagration. This was discovered in the course of research in a closely related program (6). In brief summary form, the chemical processes in HNF deflagration are as follows.

When HNF is heated to its melting point (120°C), nucleate centers of pyrolysis are formed spontaneously in random distribution throughout the fused material. These centers are initially microbubbles of gaseous decomposition products, notably  $\text{NO}_2$ . The gaseous  $\text{NO}_2$  reacts with the ambient fused material according to



Nitroform  $\text{HC}(\text{NO}_2)_3$  is unstable well below 120°C and decomposes into  $\text{NO}_2$  and residual carbon-containing products. In this way more  $\text{NO}_2$  molecules are generated than are destroyed by the above reaction, so that the gas near the gas/liquid interface is largely composed of  $\text{NO}_2$ . Molecules of  $\text{NO}_2$  diffusing back to the liquid surface repeat the reaction cycle so that gas evolution continues and the bubbles grow in volume. The reaction, being strongly exothermic, releases heat at the bubble surface which increases the temperature of the ambient fused material and thus increases the rate at which new bubble nuclei are formed. As the temperature rises, the intermediate oxygen-rich products such as  $\text{N}_2\text{O}$  and  $\text{NH}_4\text{NO}_3$  and the oxygen-lean degradation products of nitroform increasingly participate in the chemical process, which in the deflagration wave terminates in the complete transformation of the material to flame gas of more than 2700°K, comprising  $\text{N}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{O}_2$  as the principal constituents.

Additional experimental observations showed that if gaseous  $\text{NO}_2$  is passed over HNF at ambient temperature, the solid bursts into flame. At higher temperatures, if  $\text{NO}_2$  comes into contact with HNF in a confined vessel the solid explodes.

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The deflagration of HDP was found to be very similar in its essentials to that of HNF. Accordingly, an attempt was made to understand the chemistry of the process. It seemed likely that, for HDP, an oxide of chlorine played a role analogous to  $\text{NO}_2$ . A likely candidate was  $\text{ClO}_2$ , and this material was synthesized and allowed to react with HDP. The full details are given in (4). It was found that, even at  $100^\circ\text{C}$ , HDP and HP were impervious to attack by  $\text{ClO}_2$ . Hydrazine itself, however, reacted very rapidly with  $\text{ClO}_2$  at room temperature.

At this point it seemed desirable to make a thorough review of what is known of the thermal chemical behavior of hydrazine, perchloric acid and the chlorine oxides. From this it was hoped that some conceptual understanding of the chemistry of the deflagration might emerge. Highlights of this review are presented in the next section of this report. It was discovered that the mechanisms of decomposition of the chlorine oxides were almost completely unknown, hence we have undertaken some experimental work which we feel will elucidate those mechanisms. This work is reported in the following section; it is nearly but not entirely completed.



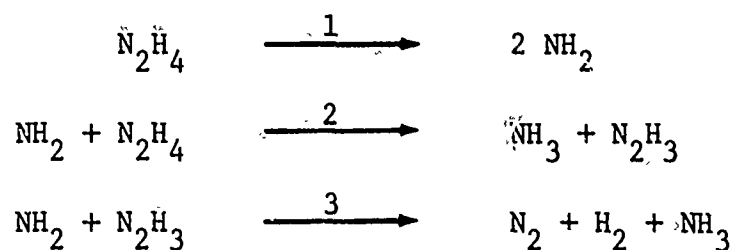
### III. REVIEW OF LITERATURE PERTINENT TO CHEMISTRY OF OXIDIZER DEFLAGRATION

#### A. HYDRAZINE AND PERCHLORIC ACID

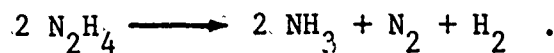
The thermal and explosive decomposition of hydrazine and the hydrazine flame have been the subject of scores of research papers. The first data on the homogeneous thermal decomposition were reported by Szwarc (7). Using the toluene carrier technique, he attempted to measure the rate of the reaction



and hence the N-N bond dissociation energy, for which he obtained the value of 60 kcal. The latest work on hydrazine decomposition was reported by McHale, Knox, and Palmer (8). Their study was done in a shock tube in the 1000°K range. In that paper, the research during the intervening years was critically reviewed, and a unifying picture of the data was presented. It was concluded that Szwarc's value of 60 kcal was at variance with the results of other investigations, particularly the flame studies. The N-N bond dissociation energy found by McHale, Knox, and Palmer was 54 kcal. The reaction was found to be first order in  $[\text{N}_2\text{H}_4]$  and showed slight total pressure dependence at 5 atm, suggesting that the reaction was not completely in the high-pressure region. The decomposition was found to proceed by a non-chain mechanism:



which yields the observed overall stoichiometry of



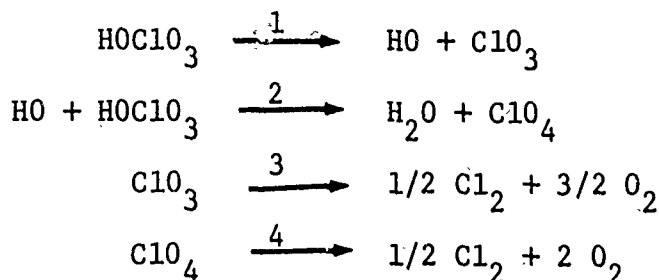
The rate constant for reaction 1 was found to be

$$k_{1\infty} = 10^{13.0} \exp(-54 \text{ kcal/RT}) \text{ sec}^{-1}$$

For completeness, we cite some of the flame studies of hydrazine. Murray and Hall (9) measured a burning velocity of 200 cm/sec for an initial temperature of 423°K and 1 atm pressure. The corresponding calculated flame temperature is 1933°K. Adams and Stocks (10) were the first to postulate a chain mechanism for the hydrazine decomposition flame reaction. Gray, *et al.* (11) obtained an activation energy of 36 kcal for the flame reaction. Finally, Kaufman and Gerri (12) studied the explosive decomposition and found that their results were very poorly reconcilable with thermal explosion theory.

It is relevant to point out that hydrazine vapor reacts rapidly with  $\text{NO}_2$  and  $\text{ClO}_2$  even at ambient temperature. Its reaction with  $\text{O}_2$ , however, is very slow, the decomposition of  $\text{N}_2\text{H}_4$  being much faster. Thus the oxidation of hydrazine by  $\text{O}_2$  is really the oxidation of its decomposition products.

The thermal decomposition of perchloric acid vapor seems to have received considerably less attention than hydrazine. The study by Levy (13) in the range 200 - 439°C defined the kinetics and mechanism very well. Above about 320°C the decomposition was homogeneous and conformed to first-order kinetics, with a rate constant  $k = 5.8 \times 10^{13} \exp(-45.1 \text{ kcal/RT}) \text{ sec}^{-1}$ . The mechanism is given as



Step 1 is rate controlling and the rate constant corresponds to that reaction. Levy calculates the  $\text{HO} - \text{ClO}_3$  bond dissociation energy to be 48.3 kcal, which value is in good agreement with the 45 kcal Arrhenius activation energy if the reaction is in the fall-off pressure regime.

Also, mention is made of the perchloric acid decomposition flame which was stabilized by Cummings and Pearson (14). They measured a burning velocity of 19 cm/sec and a flame temperature of 1080°K, both for a preheat temperature of 210°C and 1 atm pressure. The corresponding theoretical temperature was calculated to be 1076°K. However, the measured chlorine to hydrogen chloride ratio in the product gases was 0.70, versus a theoretical equilibrium ratio of 0.057.

Levy has carried out some limited experiments in which he reacted  $\text{NH}_3$  with  $\text{HClO}_4$  (15). He showed that, at 400°C, the reaction was too fast to have been controlled by the decomposition of  $\text{HClO}_4$ . Cummings and co-workers (14), moreover, showed that the dissociation of the acid is not the rate determining step in premixed fuel/acid flames (fuel = hydrogen), since the burning velocity of the self-decomposition flame of the acid is much lower than that of the fuel/acid flame at the same temperature (~1050°K). Hence, the direct attack of perchloric acid on ammonia seems likely to be the reaction route in  $\text{NH}_4\text{ClO}_4$  deflagration. Since perchloric acid decomposition is considerably faster than hydrazine decomposition, it seems certain that the direct reaction of  $\text{N}_2\text{H}_4$  and  $\text{HClO}_4$  takes place in the HP deflagration flame zone. Not so in the HDP deflagration, however, where the species entering the flame are primary products of condensed phase reactions, except possibly at pressures above 100 atm.

## B. CHLORINE OXIDES

There are four stable oxides of chlorine: chlorine monoxide,  $\text{Cl}_2\text{O}$ ; chlorine dioxide,  $\text{ClO}_2$ ; chlorine hexoxide,  $\text{Cl}_2\text{O}_6$  (which exists as  $\text{ClO}_3$  in the vapor phase); and chlorine heptoxide,  $\text{Cl}_2\text{O}_7$ . These are all endothermic compounds, potentially explosive, and must be synthesized as

used. We have prepared each of these (except  $\text{Cl}_2\text{O}$ ) many times and have had no incidents, although safety precautions must always be observed. In Appendix A, we have tabulated some thermochemical data of these molecules. What is known of the thermal behavior of these chlorine oxides and the  $\text{ClO}$  radical is discussed below.

#### 1. Chlorine Monoxide

This is a yellow gas (boiling point of liquid,  $2^\circ\text{C}$ ). Its thermal decomposition was studied by Hinshelwood and Prichard (16) and found to be homogeneous at temperatures of approximately  $120^\circ\text{C}$ . It decomposes by consecutive reactions but no mechanism could be postulated. The explosive decomposition was done by Sagulin (17). The explosion limits were measured in the range  $185 - 235^\circ\text{C}$  and 0.5 to 5 mm Hg. When  $\log P/T^2$  is plotted versus  $1/T$  a very good straight line results, which Semenov (18) uses as an example in his discussion of thermal theory of explosions. However, he also cites this as a possible example of a degenerate chain-branching explosion, since quite long (unspecified) induction times were observed.

#### 2. Chlorine Dioxide

This compound is an intense yellow gas, its red liquid boiling at  $11^\circ\text{C}$ . Schumacher and Stieger (19) studied its thermal decomposition, mainly at  $45^\circ\text{C}$ , but some experiments were performed at higher and lower temperatures. They worked in the range of 200 mm Hg pressure in quartz and Pyrex, and found the rate to be zero order and entirely dependent on the vessel surface. The effect of foreign gases was observed;  $\text{O}_2$  and  $\text{Cl}_2$  were without effect, while  $\text{Cl}_2\text{O}$  inhibited the reaction.  $\text{ClO}_3$  was observed to be an intermediate product. The  $\text{ClO}_2$  was observed to occasionally explode in some of their runs after as much as 80% decomposition. They were unable to write a mechanism for the reaction but did point out that the explosion seemed to be of the degenerate chain-branching type (20).

Booth and Bowen (21) have reported some results of the effect of light on  $\text{ClO}_2$ , but their findings are difficult to deal with. They showed that  $\text{Cl}_2\text{O}_6$  and  $\text{Cl}_2\text{O}_7$  were formed in high yield, and that photolyzed  $\text{ClO}_2$

was more sensitive to explosion than  $\text{ClO}_2$  which was not exposed to light.

Ben Caid, et al. (22) have measured the burning velocity of  $\text{ClO}_2$ ; e.g., at  $T_i = 25^\circ\text{C}$  and  $P_i = 70$  mm Hg,  $S_u = 212$  cm/sec. The calculated product gas temperature for these conditions is  $1557^\circ\text{K}$ .

### 3. Chlorine Hexoxide

The most curious of the chlorine oxides is this compound. It is a red oily liquid which freezes at  $3.5^\circ\text{C}$ . It has 0.31 mm Hg vapor pressure at  $0^\circ\text{C}$  and  $\sim 1$  mm Hg at ambient temperature (23). There have been no direct studies on its thermal stability but information on its general chemical behavior is available in a number of papers.

Goodeve and Richardson (23) degraded the vapor of  $\text{Cl}_2\text{O}_6$  completely to  $\text{Cl}_2$  and  $\text{O}_2$  and found a pressure increase of a factor of almost exactly two, for various initial pressures of vapor at ambient temperature. Thus the vapor is almost if not entirely all  $\text{ClO}_3$ , even at  $25^\circ\text{C}$ . Farquharson, Goodeve, and Richardson (24) by magnetic susceptibility measurements showed that the liquid is nearly entirely  $\text{Cl}_2\text{O}_6$ . They determined the heat of dissociation to be  $1.73 \pm .5$  kcal. Goodeve and Richardson (23) found  $\text{ClO}_3$  to be quite unstable above  $\sim -20^\circ\text{C}$ , much more so in Pyrex than quartz. For example, in a quartz vessel at ambient temperature, approximately 15-20% of  $\text{ClO}_3$  gas (no liquid) decomposed in 25 minutes.

Chlorine hexoxide has been found to be present in the photo (21) and thermal (19) decomposition of  $\text{ClO}_2$ . It is an intermediate in the photo (25) and thermal (26) chlorine-catalyzed decomposition of ozone. Its role in the  $\text{ClO}_2$  reaction is unknown, and its role in the  $\text{O}_3$  reaction is controversial. The reaction of  $\text{ClO}_2 + \text{O}_3$  to form  $\text{ClO}_3 + \text{O}_2$  was studied by Schumacher and Stieger (27). It is rapid at  $0^\circ\text{C}$  and is a practical method for preparing  $\text{ClO}_3$  or  $\text{Cl}_2\text{O}_6$ .

### 4. Chlorine Heptoxide

This is a colorless liquid, boiling at  $80^\circ\text{C}$ , with  $\sim 80$  mm vapor pressure at  $25^\circ\text{C}$ . The gas phase thermal decomposition was studied by

Figini, Coloccia, and Schumacher (28) at 100 - 120°C and at pressures of 1.5 to 80 mm Hg. The reaction is homogeneous in Pyrex and quartz and the rate constants show a falling off with pressure. They report  $k_{\infty} = 4.5 \times 10^{15} \exp(-32.9 \text{ kcal/RT}) \text{ sec}^{-1}$ , which refers to the initiation (and rate determining) reaction



Chlorine heptoxide is a product of the photodecomposition of  $\text{ClO}_2$ , apparently being formed through  $\text{ClO}_3$  intermediate (21).

#### 5. Chlorine Oxide Radical

Porter and Wright (29) have measured (using flash photolysis) the rate of the reaction



and found it to be bimolecular with  $k = 7.2 \times 10^4 \epsilon_s (\exp 0 \pm 650/\text{RT})$  l/mole-sec, where  $\epsilon_s$  is the molar extinction coefficient of  $\text{ClO}$  at 2577 Å ( $310 \leq \epsilon_s \leq 3000$ ). All known double decompositions of the above type have high activation energies (~ 28% of the sum of the energies of the bonds being broken, according to Hirschfelder's rules for an exothermic reaction). The authors seem to satisfactorily explain why this reaction is an exception.

Finally, Szabo (30) has considered the question of elementary reactions in the mechanisms for the decompositions of the chlorine oxides. His paper is no longer relevant, however, since it is based almost entirely on a value of 37 kcal/mole for the heat of formation of  $\text{ClO}$ . This value has since been determined to be 24 kcal (see Appendix A).

#### IV. EXPERIMENTAL WORK ON CHLORINE OXIDES

During the quarter we have devoted our efforts to trying to gain some understanding of the chemistry involved in oxidizer deflagration. Toward this end, the experimental work has been aimed at elucidating the mechanisms of decomposition of the chlorine oxides. We have confined our work to the oxides which seem likely to be important in oxidizers encountered in the program. These oxides are  $\text{ClO}_2$  and  $\text{ClO}_3$ . Of these two,  $\text{ClO}_2$  seemed to be the most amenable, and a study of its explosive decomposition further seemed to offer the best hope of determining its homogeneous thermal behavior. As will be seen,  $\text{ClO}_3$  is intimately involved in the  $\text{ClO}_2$  system.

##### A. APPARATUS AND PROCEDURE

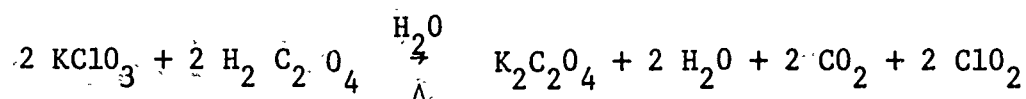
A standard apparatus for studying gas explosions were constructed. This was entirely of Pyrex and resembled in many of its essentials that described by Kaufman and Gerri (12), who verified its applicability for this type of application. It consisted of a 200 cc spherical explosion bulb, connected by 8 mm i.d. tubing and an 8 mm bore straight-through stopcock to a vacuum system. The explosion bulb was immersed in a glycerol bath, the temperature of which was controlled ( $\pm 0.1^\circ\text{C}$ ) by an American Instrument Company Bimetal Thermoregulator. This activated a relay which in turn controlled an immersion heater.

Much meaningful information can be obtained in explosion studies by equipping the explosion bulb with a pressure transducer and fine thermocouple. These allow the pressure and temperature history of the gas prior to explosion to be determined. The study was not extended to include these measurements, however.

The vacuum system consisted of storage bulbs, traps, and a mercury manometer. A vacuum of 0.1 mm Hg could be attained using a mechanical pump. All stopcocks were lubricated with Kel-F grease and the mercury

manometer was covered with a layer of Kel-F oil. No problems of attack by  $\text{ClO}_2$  or dissolving of the  $\text{ClO}_2$  in the oil or grease were encountered.

A  $\text{ClO}_2$  synthesis train was connected to the vacuum system. Chlorine dioxide was generated as needed by mixing  $\text{KClO}_3$  with moist oxalic acid and warming to about  $90^\circ\text{C}$ :



The reaction was carried out at atmospheric pressure under a slow stream of  $\text{N}_2$ . The  $\text{ClO}_2$  was passed through Drierite and Ascarite to remove most of the  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , then collected at  $-196^\circ\text{C}$ . It was finally fractionated and transferred to storage bulbs on the vacuum apparatus. Purity checks were made by measuring the vapor pressure (34) and infrared spectrum (35). No impurities were ever found, and we estimate the purity as at least within a few tenths of a percent of 100. All handling operations were carried out in near darkness and the storage bulbs were covered with black cloth bags while  $\text{ClO}_2$  was in them.

The characteristic parameter that was measured in this study was the induction time to explosion. This time was of the order of seconds to minutes, and a stopwatch was used. The procedure consisted simply of admitting  $\text{ClO}_2$  from the 0.5- or 1-liter reservoir bulb to the explosion bulb by turning the straight-through stopcock. The pressure was measured in the vacuum manifold after admission of the  $\text{ClO}_2$  and this was taken to be the pressure of  $\text{ClO}_2$  in the explosion bulb. Preliminary experiments showed that approximately 98% of the manifold pressure was realized in the bulb. The time from admission to explosion (evidenced by flash of white light) was measured. Heating times at the highest densities of this study should be of the order of tens of milliseconds (12).



## B. RESULTS

### 1. Pure $\text{ClO}_2$

Explosions of  $\text{ClO}_2$  were measured from 54 to 100°C in the pressure range of approximately 0.1 -- 0.2 to 40 mm Hg. (These very low pressures were not measured accurately but were estimated.)  $\text{ClO}_2$  was found to explode under all these conditions, with varying induction periods of 2 seconds to 18 minutes. The induction periods depended on the vessel walls but were very reproducible from experiment to experiment if no change in the surface was allowed to occur. In Figure 1, induction periods as a function of pressure are shown for four runs at temperatures of 62° to 100°C. It is seen that the condition of the surface is much more important than temperature. Between the runs at 100, 80 and 62°C, the surface was unchanged. Between these runs and the run at 74°C, however, the explosion bulb had been filled with atmospheric air then pumped on at 110°C for several hours.

These curves bear a striking resemblance to Langmuir adsorption isotherms. If we consider a surface initiation reaction is controlling the time to explosion, then at high pressures the surface is saturated with adsorbed molecules and the induction time is independent of pressure. At low pressures the induction time depends very strongly on pressure, since the amount of adsorbed reactant depends on reactant gas-phase concentration. But in Figure 2, the general shape of the curves is seen to reverse itself at lower temperature. A check was performed on whether these lower-temperature curves represented spurious results, e.g., by some "cleaning up" of the surface with each successive run. The data on curve 2 were obtained immediately after those on curve 1. The same effect is seen to be observed with slightly longer induction periods.

### 2. Effect of Added Gases

Mixtures of equal pressures of  $\text{ClO}_2$  with  $\text{N}_2$ ,  $\text{Cl}_2$ , and  $\text{O}_2$  were made and the effect of these added gases was determined. The results are shown in Figure 3. A promotion effect is observed below a certain pressure, its magnitude varying only slightly from gas to gas. (In other experiments,

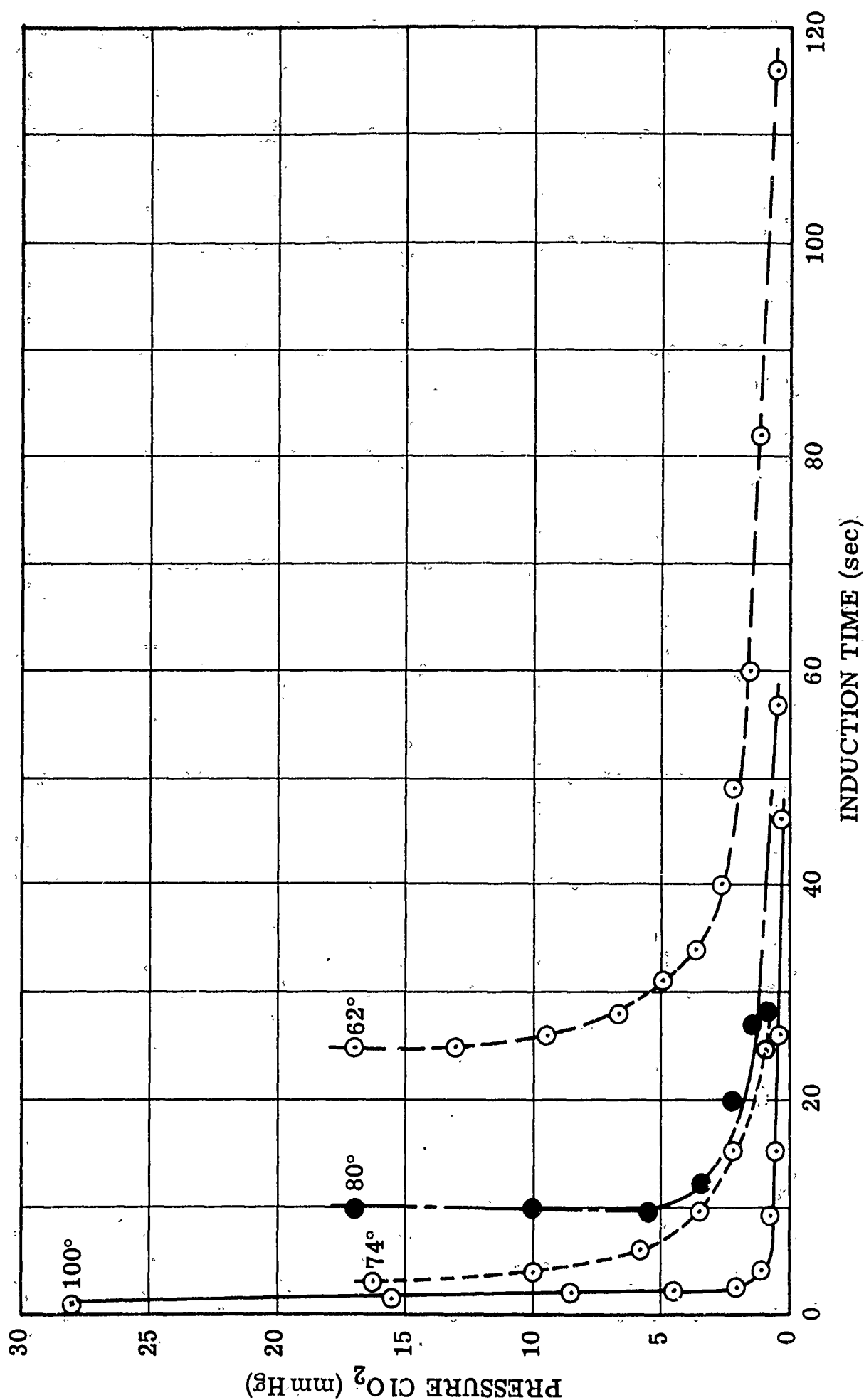


Figure 1. Induction Times for Explosions of  $\text{ClO}_2$  as a Function of Pressure.

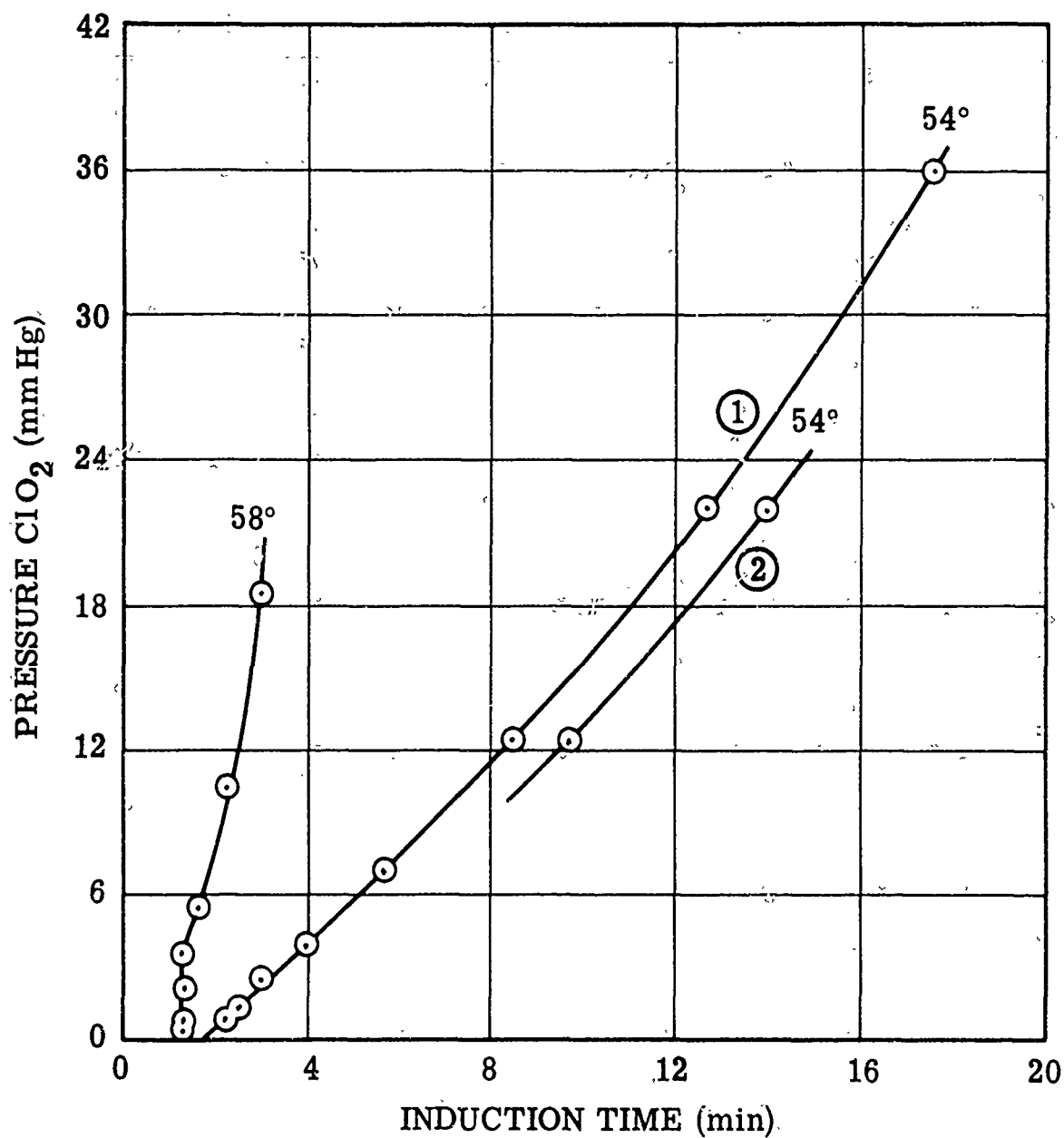


Figure 2. Induction Times for Explosions of  $\text{ClO}_2$  as a Function of Pressure.

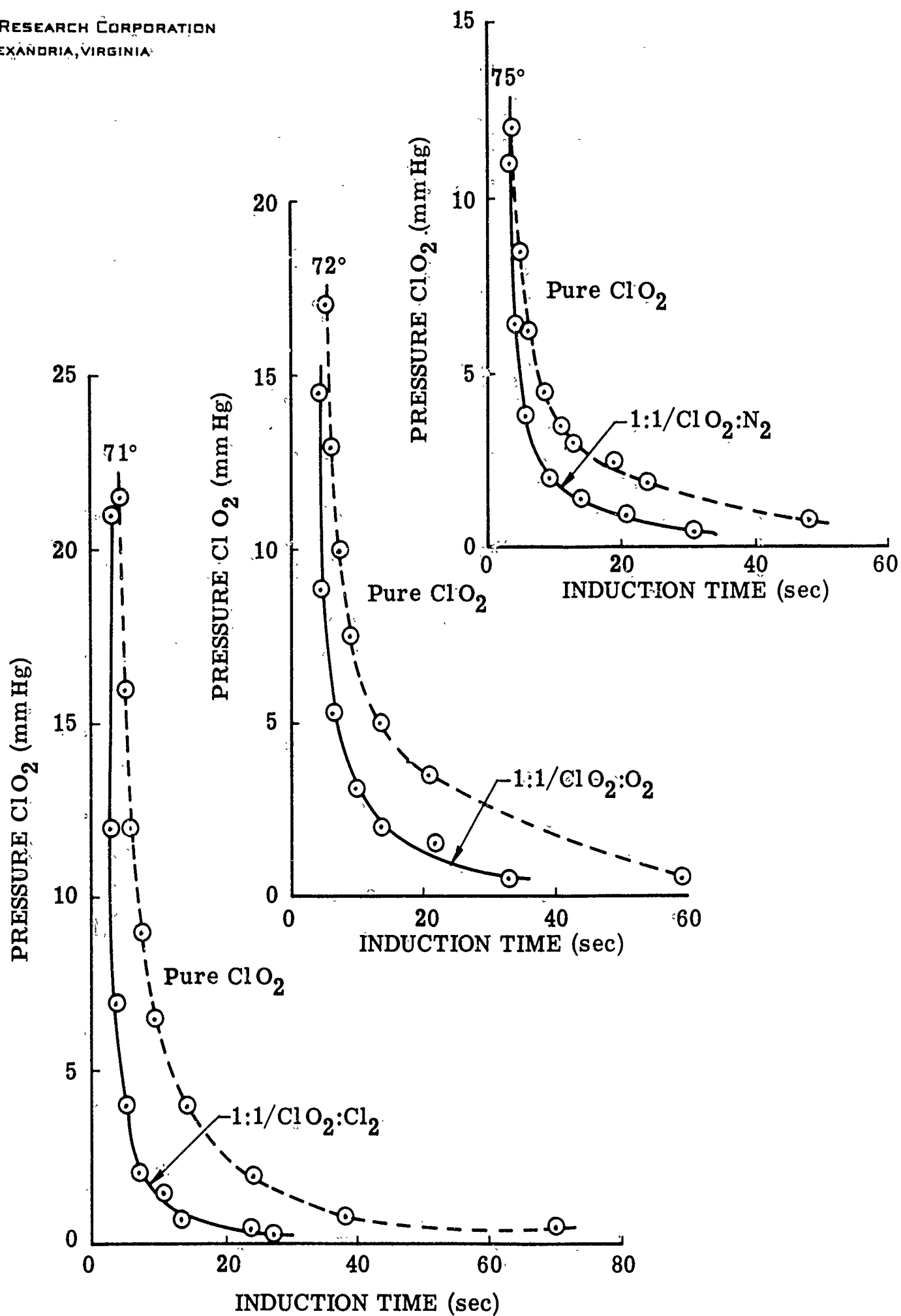
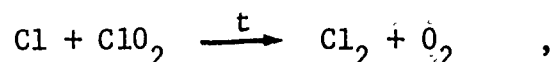
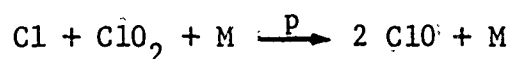


Figure 3.- Effect of Added Gases on Induction Periods for  $\text{ClO}_2$  Explosions.

we have determined that the effect of  $O_2$  and  $N_2$  is exactly the same from 20 to 35 mm Hg.) It was necessary to carry out these experiments in the following way: Two reservoir bulbs were used, one filled with pure  $ClO_2$  and one filled with a 50-50 mixture of  $ClO_2$ -foreign gas. Alternate explosions were made using first the  $ClO_2$  then the mixture. This was the best method of obtaining results that could be compared.

The promotion of the explosion, i.e., the reduction of the time to explosion at a given pressure of  $ClO_2$ , can be ascribed to the impeding of the diffusion of radicals to the vessel walls where they would be destroyed. This inhibition of wall termination reaction allows radicals to spend longer times in the body of the gas where they react to form an intermediate, whose critical concentration is reached sooner. An alternate explanation of the promotion effect - enhancing of termolecular propagation reactions - must be rejected, since the effect decreases with increasing pressure. If, for example, we hypothesize the following reaction couple as important,

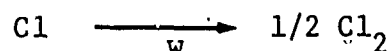


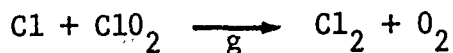
then added gas would promote the explosion. However, since the ratio

$$\frac{\text{rate propagation}}{\text{rate termination}} = \frac{k_p}{k_t} [M]$$

the promotion would be relatively large at high pressure and decrease as pressure decreases. This is the opposite of what is observed.

The vanishing of the promotion effect at high pressure is due to gas-phase termination replacing wall termination as the important reaction. Again, as a hypothetical example, if the reactions





were important termination reactions,

$$\frac{\text{rate gas-phase reaction}}{\text{rate wall reaction}} = \frac{k_g}{K_w} [\text{ClO}_2] .$$

(This ratio actually increases as the square of  $[\text{ClO}_2]$ , since  $K_w$  is inversely proportional to total gas concentration.)

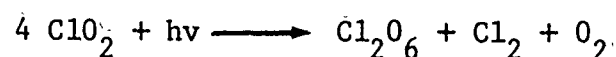
### 3. Effect of Other Chlorine Oxides

Explosions of the type observed here with very long induction periods are of a type known as degenerate chain-branching explosions (18). They involve a stable intermediate, and the induction period is associated with the build-up of this intermediate to a critical concentration. This intermediate is necessarily another chlorine oxide, although it could conceivably be a presently unknown one. The possibility of the intermediate being  $\text{Cl}_2\text{O}$  was ruled out by the work of Schumacher and Stieger (19), who added  $\text{Cl}_2\text{O}$  in high concentration to  $\text{ClO}_2$  and found inhibition. We have decomposed  $\text{ClO}_2$  and carefully analyzed the products in order to determine the intermediate. Below is described one such experiment.

Fifty mm Hg pressure of  $\text{ClO}_2$  in 1 liter volume at  $28^\circ\text{C}$  were allowed to decompose for several days to approximately 50% extent. The experiment was carried out in total darkness as was subsequent handling. The  $\text{Cl}_2$  and  $\text{O}_2$  products were separated and the remaining  $\text{ClO}_2$  and other products were concentrated in an infrared cell and the spectrum taken with five times amplification. The only bands not belonging to  $\text{ClO}_2$  were due to  $\text{Cl}_2\text{O}_7$  (36). No  $\text{Cl}_2\text{O}$  (37) or  $\text{ClO}_3$  (spectrum unreported in literature) bands or any other bands were found. This suggests  $\text{Cl}_2\text{O}_7$  as the intermediate, but does not exclude  $\text{ClO}_3$ , since the latter could have been converted to  $\text{Cl}_2\text{O}_7$  in the IR cell, or could have decomposed as fast as it was formed in the Pyrex vessel at  $28^\circ\text{C}$  over a 6-day period. Accordingly, we have determined the effect of  $\text{Cl}_2\text{O}_7$  and  $\text{ClO}_3$  on the explosion.

$\text{Cl}_2\text{O}_7$  was synthesized by dehydrating  $\text{HClO}_4$  (70%) with excess  $\text{P}_2\text{O}_5$  (38). Its vapor pressure was checked against the literature value (38). Two percent  $\text{Cl}_2\text{O}_7$  was added to  $\text{ClO}_2$  and the explosion curve determined versus that for pure  $\text{ClO}_2$ . These data are shown in Figure 4, where it is clear that  $\text{Cl}_2\text{O}_7$  does not significantly affect the induction time.

$\text{ClO}_3$  was synthesized by irradiating  $\text{ClO}_2$  with ultraviolet light. This was done in a 500cc spherical bulb, the lower half of which was kept at  $-45^\circ\text{C}$ . Fifteen mm Hg pressure  $\text{ClO}_2$  were decomposed in this way, the  $\text{ClO}_3$  being frozen (as  $\text{Cl}_2\text{O}_6$ ) on the vessel walls as it formed. The approximate stoichiometry was determined as (assuming no  $\text{Cl}_2\text{O}_7$  formation):



After complete reaction the bulb was pumped out at  $-45^\circ\text{C}$ , which removed all other products except  $\text{Cl}_2\text{O}_6$ . The red oily liquid has approximately 1 mm Hg vapor pressure at room temperature.

Fifty mm Hg pressure  $\text{ClO}_2$  were added to the bulb containing the  $\text{Cl}_2\text{O}_6$ . This represented a mixture of 2%  $\text{ClO}_3$  in  $\text{ClO}_2$  since red liquid was still present. Explosion experiments were performed immediately with this mixture and with an equal amount of pure  $\text{ClO}_2$  whose induction times were approximately 90 seconds at  $60^\circ\text{C}$ . When the mixture containing 2%  $\text{ClO}_3$  was admitted to the explosion vessel the induction period was completely eliminated, so much so that before the stopcock could be turned through the open position the explosion flashed back through the manifold and into the reservoir bulb. With  $\text{ClO}_3$  thus established as the intermediate, we plan some limited experiments to try to determine the approximate concentration level at which the induction time is eliminated.

#### 4. Memory Experiments and Effect of Irradiation

Two other types of experiments bearing on the problem were performed. In the first it was found that  $\text{ClO}_2$  is much more sensitive to explosion if it is previously irradiated. For example, 10 mm Hg pressure

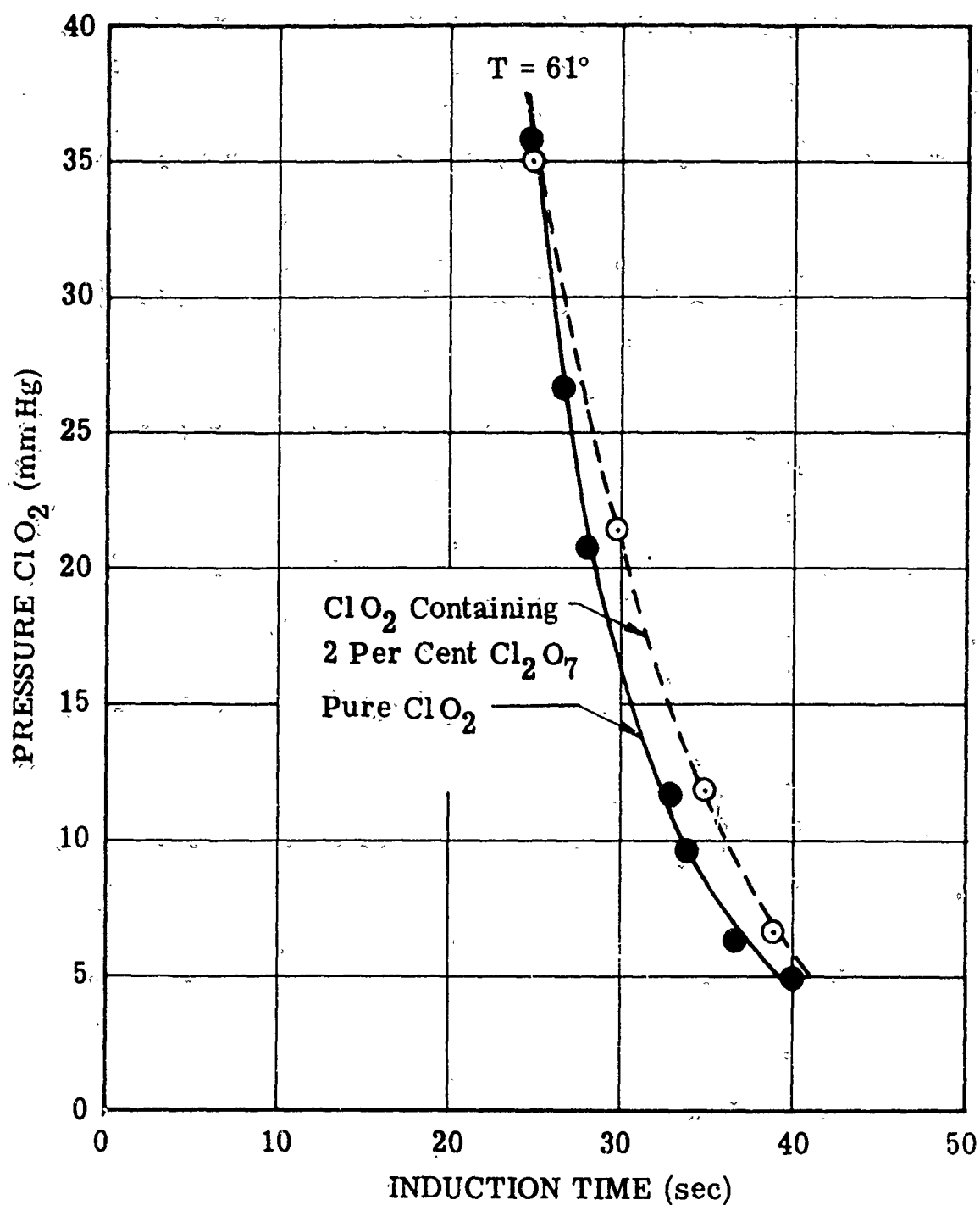


Figure 4. Effect of 2 Per Cent  $\text{Cl}_2\text{O}_7$  on Induction Times for  $\text{ClO}_2$  Explosions.



of pure  $\text{ClO}_2$  exploded with an induction period of 77 seconds and upon being exposed to low intensity UV light, through Pyrex, for 2 minutes, this induction time was reduced to 10 seconds. Further irradiation reduced the time more, but  $\text{ClO}_2$  never exploded at room temperature regardless of the radiation.

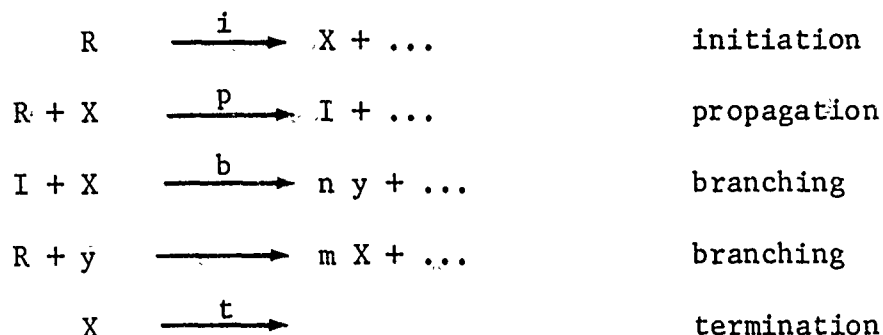
Another experiment was carried out to determine whether the  $\text{ClO}_2$  explosion system had a "memory." During a series of explosions, the reactor was removed from the temperature bath ( $59^\circ\text{C}$ ) and cooled to room temperature for 5 minutes. It was then put back into the bath and the times involved were measured. Without removal, the induction period would have been 100 seconds. The  $\text{ClO}_2$  was allowed to react for 90 seconds then removed for 5 minutes. When it was replaced the additional induction time would have been 10 seconds if it had a perfect memory. It would have been 100 seconds or more if it had no memory. The time observed was 40 seconds, indicating that the system had an imperfect memory.

Both of the foregoing experiments are consistent with  $\text{ClO}_3$  as an intermediate and what is known of its behavior (21, 23).

### C. DISCUSSION

This brief discussion is confined to some general remarks on the type of explosive behavior observed in this study, the detailed application to  $\text{ClO}_2$  being deferred for the present.

As was mentioned previously, the explosion of  $\text{ClO}_2$  is of a degenerate chain-branching type involving the formation of a stable intermediate. This type of reaction system must follow a general scheme, which must in its essentials resemble the following:



Here R = reactant; x and y = highly reactive species (radicals); I = stable intermediate; n and m  $\geq 1$ , but n.m  $\geq 3$  for explosion.

For such a scheme, the steady-state approximation will hold for [X] and [y], but not for [I]. Thus (where n.m =  $\alpha$ );

$$\frac{d[I]}{dt} = k_i[R] - \frac{k_p[R] - k_b[I]}{k_t + k_p[R] - (\alpha - 1)k_b[I]}$$

Ignoring  $k_t$  in the above equation, as [I] increases and [R] decreases, the denominator will approach zero faster than the numerator, since the factor  $(\alpha - 1) \geq 2$ . The termination reaction slows the approach to  $[I]_{\text{critical}}$  and can prevent explosion under certain conditions. The critical concentration of intermediate is (again ignoring  $k_t$ )

$$[I]_{\text{crit}} = \frac{1}{(\alpha - 1)} \frac{k_p}{k_b} [R]$$

The steady-state concentration of intermediate would be

$$[I]_{ss} = \frac{k_p}{k_b} [R]$$

Hence, the system explodes when some fraction,  $\frac{1}{\alpha - 1}$ , of the steady-state concentration is reached.

For the  $\text{C}_2\text{H}_2$  system, elementary reactions of the mechanism must be chosen which will yield a proper rate equation. Upon integration (from 0 to  $\tau$  in time, and 0 to  $[I]_{\text{crit}}$  in concentration) an expression must result which reproduces the experimental pressure-induction time curves and the other experimental data.

## V. PLANS FOR FUTURE WORK

A limited number of experiments remains to be done on the  $\text{ClO}_2$  system, and the final interpretation of the results must be completed. Efforts are then going to be devoted to studies on the quenching of deflagration by pressure decay.

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APPENDIX A

THERMOCHEMICAL DATA FOR CHLORINE OXIDES

SPECIES	$\Delta H_f^\circ$ (298°K) (kcal/mole)	$D_o^\circ$ (kcal/mole)	REFERENCE
O	59.6	-	31
O <sub>2</sub>	0	118.0	31
O <sub>3</sub>	34.1	24.2	31
Cl	28.9	-	31
ClO	24.2	63.33	31
ClO <sub>2</sub>	25 ± 1.5	57.5 (a)	31
ClO <sub>3</sub>	37 ± 2 (288°)	46 (a)	32
Cl <sub>2</sub>	0	57.04	31
Cl <sub>2</sub> O	18.1 ± .3	33 (a)	31
Cl <sub>2</sub> O <sub>6</sub>	72.3 (c)	1.73 ± .5 (b)	24
Cl <sub>2</sub> O <sub>7</sub>	63.4 ± 3 (290°)	-	32
HClO <sub>4</sub>	-1.7 (d)	46 (e)	14, 33

(a) Estimated from heats of formation at 298°K.

(b) This value is the reported (24) dissociation energy for  
Cl<sub>2</sub>O<sub>6</sub> → 2 ClO<sub>3</sub>.

(c) Calculated from (b) and  $\Delta H_f$  for ClO<sub>3</sub>.

(d) The average from references 14 and 33.

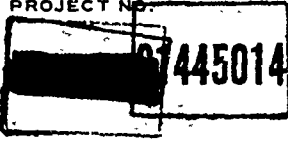
(e) Estimated from (d) and heats of formation for ClO<sub>3</sub> and  
OH (See (31)); refers to HO - ClO<sub>3</sub>.

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		2b. GROUP	
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13. ABSTRACT  The task of the present program is fundamental research on advanced solid oxidizers with the aim of understanding their self-deflagration. Hydrazine perchlorate and hydrazine diperchlorate have received, of late, most of the attention. The effort during this quarter has been devoted to elucidating some of the chemistry involved in the deflagration process. Toward this end we have carried out a literature review of the thermal behavior of hydrazine and perchloric acid. This was extended to include a review of reactions of chlorine oxides. The kinetics and mechanisms of the latter compounds, it was discovered, are not very well understood. Hence, we have performed some experiments on ClO <sub>2</sub> and ClO <sub>3</sub> , two species which seem likely to be important in oxidizers encountered in the program. In particular we have concentrated on the explosive decomposition of ClO <sub>2</sub> . It was found to explode by a degenerate chain-branching mechanism at all temperatures and pressures above 54°C and a few tenths of a mm Hg. Very long induction periods were observed, and ClO <sub>3</sub> was shown to be a critical intermediate. The explosion is promoted by irradiation and by addition of foreign gases.			

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Deflagration High-Energy Solid Oxidizers Solid Oxidizers Chlorine Oxides Hydrazine Perchlorate Hydrazine Diperchlorate						

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